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# Emitting-tunable $\text{Eu}^{(2+/3+)}$ -doped $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2$ apatite phosphor for n-UV WLEDs with high-color-rendering

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Currently, developing single-phased white light phosphors based on a single-doped activator is an efficient approach to blends of bicolor/tricolor phosphors for realizing phosphor-converted white light emitting diodes (pc-WLEDs) with a high color rendering index (CRI) and low correlated color temperature (CCT). Here, we present high CRI ( $R_a = 93-95$ ) and low CCT (3500–6000 K) white lights by cosubstituting  $[\text{Ca}^{2+}-\text{P}^{5+}]$  for  $[\text{La}^{3+}-\text{Si}^{4+}]$  in the solid solution  $\text{Ca}_{(8-2)}\text{La}_{(2-8)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:\text{Eu}^{2+}/\text{Eu}^{3+}$  (CLPSO\_Eu). The results are attributed to the presence of multi  $\text{Ca}^{2+}$  sites due to possible mixing nanophases and the simultaneous occupancy of  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  sites by Eu, resulting in the mixing of blue (466 nm) and green emissions (540 nm) for  $\text{Eu}^{2+}$ , and red emission (613 nm) for  $\text{Eu}^{3+}$ , which were perfectly confirmed using X-ray Rietveld refinement, photoluminescence spectra and extended X-ray absorption fine structure. These findings not only imply that the as-prepared CLPSO\_Eu are promising single-phased white light phosphor for near-UV based WLEDs but also offer a novel avenue to design high CRI white light phosphors based on a tunable  $\text{Eu}^{2+}/\text{Eu}^{3+}$ .

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## 1. Introduction

Near ultraviolet (n-UV) based white light-emitting diodes (WLEDs) that are composed of 380–420 nm LED chips and bicolor/tricolor phosphors are emerging as promising high CRI and low CCT lighting sources.<sup>1–5</sup> Unfortunately, this type of WLED easily suffers from a complicated fabrication process and color unbalance. An available alternative is to develop single-phased white light phosphors.<sup>6</sup> The common single-phased white light infers the energy transfer among activator ion pairs such as  $\text{Ce}^{3+}/\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ ,  $\text{Ce}^{3+}/\text{Eu}^{2+} \rightarrow \text{Tb}^{3+}$ ,  $\text{Mn}^{2+}$ .<sup>7–10</sup> However, the  $\text{Mn}^{2+}$  red emission belongs to weak d–d transitions, resulting in the low luminescence efficiency and poor thermal stability.<sup>11</sup> To reduce the energy loss in the energy transfer process, single-activator-doped white light phosphors are highly desired, in which the emission spectra of the single activator must cover the entire visible light range.<sup>12</sup>  $\text{Eu}^{2+}$  is one of the most popular activators and its 4f–5d transition can be tuned from 400 to 700 nm depending on its coordination

environment.<sup>13–18</sup> Recently, single  $\text{Eu}^{2+}$ -activated materials were designed as single-phased white light phosphors by changing host component, such as  $\text{Sr}_5(\text{PO}_4)_{3-x}(\text{BO}_3)_x\text{Cl}:\text{Eu}^{2+}$ .<sup>12</sup> However, to obtain enough full width at half maximum (FWHM) of  $\text{Eu}^{2+}$  emission is still a challenge. Especially, more red component should be covered for presenting high CRI white light.<sup>19</sup>  $\text{Eu}^{3+}$ -activated materials are potential red-emitting phosphors in pc-WLEDs due to the typical 4f–4f transitions ( $^5\text{D}_{0,1}-^7\text{F}_J, J = 0-6$ ) in the range of 570–700 nm from  $\text{Eu}^{3+}$ .<sup>20–22</sup> Moreover, cation substitution has been confirmed as an effective strategy to adjust luminescent colors and properties of phosphor materials.<sup>23–31</sup> In the previous study, we have demonstrated the color-tunable emission from blue or green light to red light based on the valance transformation (3+ to 2+) through cation cosubstitution.<sup>32</sup> However, there are few reports to present single-phased white light emission based on simultaneously blue, green, red-emitting  $\text{Eu}^{2+}/\text{Eu}^{3+}$ -activated phosphors. Herein, we realize high CRI white lights with low correlated color temperatures by cosubstituting  $[\text{La}^{3+}-\text{Si}^{4+}]$  for  $[\text{Ca}^{2+}-\text{P}^{5+}]$  in the solid solution  $\text{Ca}_{(8-2)}\text{La}_{(2-8)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:\text{Eu}^{2+}/\text{Eu}^{3+}$ .

## 2. Experimental section

### Chemicals and materials

$\text{CaCO}_3$  (Aldrich,  $\geq 99.95\%$ ),  $\text{La}_2\text{O}_3$  (Aldrich,  $\geq 99.999\%$ ),  $\text{SiO}_2$  (Aldrich,  $\geq 99.995\%$ ),  $(\text{NH}_4)_2\text{HPO}_4$  (Aldrich,  $\geq 99.9\%$ ), and  $\text{Eu}_2\text{O}_3$  (Aldrich,  $\geq 99.999\%$ ) were purchased from Sigma-Aldrich Corporation. All of the initial chemicals were used

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without further purification. Aluminum oxide crucibles were used to sinter the phosphor samples.

## Preparation

A series of  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  ( $x = 0-6$ ) compounds were prepared by a conventional high-temperature solid state reaction. The doping concentration of Eu was fixed at 2 atom.% of Ca/La. All samples were synthesized in a reductive atmosphere and  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  ( $0 \leq x \leq 6$ ) samples were correspondingly denoted as CLSPO- $x$  ( $x = 0-6$ ). Stoichiometric amounts of  $\text{CaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and  $\text{Eu}_2\text{O}_3$  were thoroughly mixed and pestled in an agate mortar for 1 h. Then, the powder mixtures were placed in aluminum oxides crucibles and sintered in a horizontal tube furnace at  $1300^\circ\text{C}$  for 8 h with a reducing atmosphere of  $\text{H}_2$  (8%) and  $\text{N}_2$  (92%) atmosphere. After the furnace slowly cooled to room temperature, the sintered products were grinded again, generating the final phosphor powders. The as-prepared  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  ( $x = 0, 1, 2, 3, 4, 5, 6$ ) samples were denoted as CLSPO-0, 1, 2, 3, 4, 5, and 6, respectively. Phosphor-converted solid-state lighting devices were fabricated around discrete UV LEDs by using gold wires for electrical operation. The LEDs emit with  $\lambda_{\text{max}} = 395 \text{ nm}$ . Homogeneous mixtures of the as-prepared phosphors and transparent silicone resin were cured on the LED chip. After the packaging was completed, the optical properties of the device were measured in an integrating sphere under forward DC bias conditions.

## Characterization

Finely ground powders were used in all of the measurements. The phase purity of all samples were analyzed using X-ray diffraction (XRD) obtained in a D8 Focus diffractometer (Bruker, Karlsruhe, Germany) at a scanning rate of  $1^\circ \text{ min}^{-1}$  in the  $2\theta$  range from  $5^\circ$  to  $120^\circ$ , and the counting time was 5 s per step with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). XRD Rietveld profile refinements of the structural models and texture analysis were performed with the use of General Structure Analysis System (GSAS). The photoluminescence measurements were recorded with a Fluoromax-4P spectrophotometer (Horiba Jobin Yvon, New Jersey, USA) equipped with a 450 W xenon lamp as the excitation source. Both excitation and emission spectra were set up to be 1.0 nm with the width of the monochromator slits adjusted as 0.50 nm. XANES of Eu  $\text{L}_3$  edge was recorded with a wiggler beamline BL17C (the synchrotron X-ray diffraction wavelength  $\lambda = 0.774907 \text{ \AA}$ ) at National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The thermal stability of luminescence of phosphor materials were measured by Fluoromax-4P spectrometer connected a heating equipment (TAP-02). The Commission Internationale de l'Eclairage chromaticity color coordinates, color rendering index ( $R_a$ ), and CCT of WLED devices were measured by Starspec SSP6612.

## 3. Results and discussion

The crystal structure and phase purity of the studied samples were confirmed by powder X-ray diffraction (XRD). Fig. 1a shows

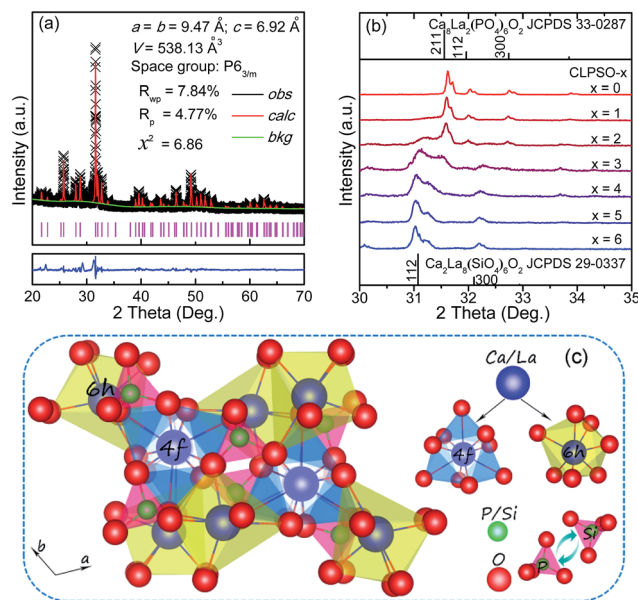


Fig. 1 The Rietveld XRD refinement of (a)  $\text{Ca}_{5.88}\text{La}_{3.92}\text{Eu}_{0.2}(\text{PO}_4)_4(\text{SiO}_4)_2\text{O}_2$  sample by the GSAS program, and (b) enlarged XRD patterns at  $2\theta = 30-35^\circ$  of  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  (CLSPO- $x$ ) ( $x = 0-6$ ) samples. Observed and calculated XRD patterns, baseline, and their difference are depicted with black crosses, red solid line, green solid line, and blue solid line, respectively. The short vertical lines show the positions of Bragg reflections of the calculated pattern. (c) A schematic crystal structure and cation-cosubstitution of CLSPO- $x$  along  $c$ -axis.

the Rietveld XRD refinement of the representative  $\text{Ca}_{5.88}\text{La}_{3.92}\text{Eu}_{0.2}(\text{PO}_4)_4(\text{SiO}_4)_2\text{O}_2$  (CLSPO-2) sample.<sup>33</sup> The refined structure parameters indicate that the studied sample crystallizes in hexagonal phase with space group  $P6_3/m$  (176),  $a = b = 9.47 \text{ \AA}$ ,  $c = 6.92 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 538.13 \text{ \AA}^3$  and  $Z = 1$ . The atom positions, fraction factors, and thermal vibration parameters were refined by convergence and satisfied well the reflection conditions,  $R_{\text{wp}} = 7.84\%$ ,  $R_p = 4.77\%$ , and  $\chi^2 = 6.86$ . The results imply the formation of single-phased solid solution (CLSPO-2). Fig. 1b shows the XRD patterns for  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  ( $0 \leq x \leq 6$ ) samples at  $30-35^\circ$ . The XRD patterns of  $x = 0$  and  $x = 6$  samples can be well assigned to the standard  $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$  (CLPO, JCPDS no. 33-0287) and  $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$  (CLSO, JCPDS no. 29-0337) phases, respectively.<sup>34,35</sup> A linear shift of XRD diffraction peaks at  $30-35^\circ$  to small-angle direction with the substitution of  $[\text{Ca}^{2+}-\text{P}^{5+}]$  for  $[\text{La}^{3+}-\text{Si}^{4+}]$  (Fig. 1b) is attributed to the smaller ion radius of  $r$   $[\text{Ca}^{2+}-\text{P}^{5+}]$  ( $1.23 \text{ \AA}$ , CN = 7;  $1.35 \text{ \AA}$ , CN = 9) than that of  $r$   $[\text{La}^{3+}-\text{Si}^{4+}]$  ( $1.36 \text{ \AA}$ , CN = 7;  $1.476 \text{ \AA}$ , CN = 9). This phenomenon not only indicates the successful incorporation of  $[\text{La}^{3+}-\text{Si}^{4+}]$  into the lattice by substituting  $[\text{Ca}^{2+}-\text{P}^{5+}]$  but also confirms that the CLSPO- $x$  ( $x = 0-6$ ) can maintain single phase and form solid solutions in the whole series.<sup>32</sup> Interestingly, two (112) crystal planes that respectively belong to CLPO and CLSO hosts simultaneously appear in CLSPO-2 and CLSPO-3 samples. This finding imply a possible mixing nanophases of two crystal structures, which could induce the coexistence of different coordination environments for activator ions.<sup>23</sup> A schematic



spatial view of the  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_6-x(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  solid solution unit cell is shown in Fig. 1c. Ca/La/Eu occupy the nine-coordinated 4f sites with  $C_3$  point symmetry and the seven-coordinated 6h sites with  $C_s$  point symmetry.<sup>33–35</sup> Along the  $c$ -axis,  $\text{Ca/LaO}_9$  tetrakaidecahedron chains at 4f sites share faces, while  $\text{Ca/LaO}_7$  decahedrons at 6h sites share vertexes and edges. The neighbouring tetrakaidecahedron and decahedron are connected through tetrahedral  $\text{PO}_4$  groups and share edges. With the substitution of  $\text{Si}^{4+}$  for  $\text{P}^{5+}$ , the relative  $\text{Ca}^{2+}/\text{La}^{3+}$  ratio will change according to the charge compensation principle, accompanying the site change of the Eu activator at  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  sites.

Fig. 2a and b depict the normalized photoluminescence excitation (PLE) and emission spectra (PL) of CLPSO- $x$  samples prepared at 1300 °C. In previous report, it was found that the PL properties of  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$  phosphors were related to the synthesis temperature.<sup>23,32</sup> The  $\text{Eu}^{2+}$  ions in  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$  exhibit blue emission (400–600 nm) and green emission (420–650 nm) when the sintering temperatures are 1250 °C and 1350 °C, respectively.<sup>32,33</sup> The current CLPSO-0 sample show a broad absorption band from 250 nm to 500 nm centered at 395 nm due to the typical 5d–4f transitions of  $\text{Eu}^{2+}$ . Interestingly, under 395 nm UV excitation, it gives a super wide emission band from 420 nm to 700 nm with two emission centers at 467 nm and 556 nm, respectively. Obviously, this super wide emission band also originates from the 5d–4f transitions of  $\text{Eu}^{2+}$  ions, and it simultaneously contains the  $\text{Eu}^{2+}$  emissions of  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$ -1250 °C and  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$ -1350 °C. The results reveal that two kinds of  $\text{Eu}^{2+}$  lattice environments appear in CLPSO-0 host at an intermediate sintering temperature (1300 °C). According to the previous conclusions in  $\text{Eu}^{2+}$ -doped  $(\text{Sr}_{1-x}\text{Ba}_x)\text{Si}_2\text{O}_7$  system, the super wide  $\text{Eu}^{2+}$  emission in  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$ -1300 °C single-phased sample should be attributed to the nanophase segregation and mixing  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$ -

1250 °C and  $\text{Ca}_{7.84}\text{La}_{1.96}\text{Eu}_{0.2}(\text{PO}_4)_6\text{O}_2$ -1350 °C phases, which is consistent with the XRD results.<sup>23</sup> It is noted that some previous report also ascribed the same wide  $\text{Eu}^{2+}$  emission to replace at two different sites. It maybe the complexes of the two situation. Although the emission spectrum of CLPSO-0 sample covers a wide range from 420 nm to 700 nm, it's CIE color coordinates (0.316, 0.386) locates at yellow-green junction region due to the deficiency of red component. In addition, there is no obvious characteristic emission of  $\text{Eu}^{3+}$ , revealing that Eu mainly occupy the lattice sites of  $\text{Ca}^{2+}$  ions and thus present +2 form. Interestingly, the  $\text{Eu}^{2+}$  emission gradually decreases and the characteristic red emissions of  $\text{Eu}^{3+}$  that are assigned to  ${}^5\text{D}_0$ – ${}^7\text{F}_{0-3}$  transitions, *i.e.*, 577 nm (0–0), 588 nm (0–1), 613 nm (0–2), 650 nm (0–3), 700 nm (0–4), appear and gradually rise with increasing  $[\text{La}^{3+}\text{--}\text{Si}^{4+}]$  concentration. Moreover, the enhanced relative emission intensity of  $\text{Eu}^{3+}/\text{Eu}^{2+}$  with increasing  $x$  value, implying a gradual transformation from  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  with the substitution of  $[\text{La}^{3+}\text{--}\text{Si}^{4+}]$  for  $[\text{Ca}^{2+}\text{--}\text{P}^{5+}]$ . Beyond  $x \geq 2$ , the emission intensity of  $\text{Eu}^{3+}$  is obviously higher than that of  $\text{Eu}^{2+}$ . Finally, at  $x = 6$  the  $\text{Eu}^{2+}$  emission vanishes, and only the characteristic emission of  $\text{Eu}^{3+}$  can be observed. The result indicates that the Eu mainly enter into the  $\text{La}^{3+}$  sites in  $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$  parent lattice and show +3 form. When monitoring with the maximum emission at 613 nm ( ${}^5\text{D}_0$ – ${}^7\text{F}_2$ ), the PLE spectra of  $x = 3$ –6 samples mainly consist of a  $\text{O}_{2p} \rightarrow \text{Eu}_{4f}$  charge transfer band (CTB) in 250–335 nm and several 4f–4f transition lines from 350 nm to 500 nm.<sup>19</sup> Especially, the excitation intensities of  ${}^7\text{F}_0$ – ${}^5\text{L}_6$  (395 nm) and  ${}^7\text{F}_0$ – ${}^5\text{D}_2$  (463 nm) transitions are almost equivalent to or even surpass the  $\text{O}_{2p} \rightarrow \text{Eu}_{4f}$  CTB absorption intensity, revealing that these samples could be effectively excited by 395 nm n-UV and 463 nm blue light. In general, the transformation of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  happens with the substitution of  $[\text{Ca}^{2+}\text{--}\text{P}^{5+}]$  for  $[\text{La}^{3+}\text{--}\text{Si}^{4+}]$  in the CLPSO- $x$  host, in which the  $\text{Eu}^{2+/3+}$  can coexist and be controllably adjusted at appropriate  $x$  value. The finding leads to the emission colors of the studied samples from yellow-green region to red light across the white light region, as shown by the luminescence photos in Fig. 2c. The CIE color coordinates of CLPSO- $x$  samples are listed in Table 1 and Fig. 3. Evidently, the color coordinates gradually shift from (0.316, 0.386) to (0.618, 0.383), further confirming the tunable emission colors. Especially, the  $x = 2$ –4 are well distributed at different white light region with the different ratio of  $\text{Eu}^{2+}/\text{Eu}^{3+}$ , which could be used as potential

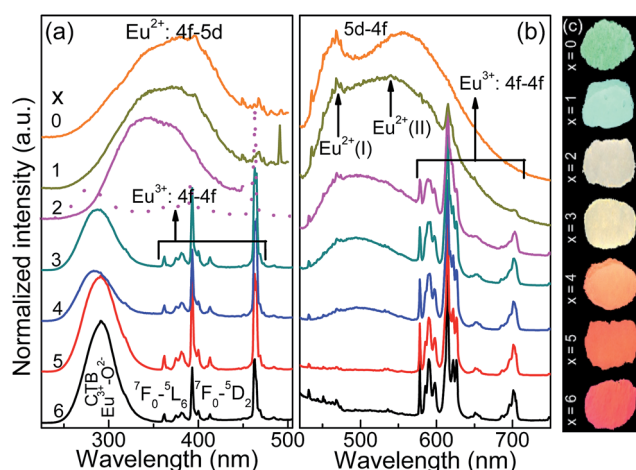


Fig. 2 (a) The normalized photoluminescence excitation (PLE,  $\lambda_{\text{em}} = 466, 556, 613$  nm) and (b) emission (PL,  $\lambda_{\text{ex}} = 395$  nm) spectra of CLPSO- $x$  ( $x = 0$ –6) samples prepared at 1300 °C. (c) The luminescent photos of CLPSO- $x$  ( $x = 0$ –6) samples under 395 nm UV are also shown.  $\text{Eu}^{2+}(\text{I})$  and  $\text{Eu}^{2+}(\text{II})$  means the crystal lattice environments of blue and green emission, respectively.

Table 1 CIE color coordinates and emission positions of  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_6-x(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  (CLPSO- $x$ ) ( $0 \leq x \leq 6$ ) prepared at 1300 °C, respectively ( $\lambda_{\text{ex}} = 395$  nm)

Sample	X	Y	Peak (nm)
$x = 0$	0.316	0.386	468
$x = 1$	0.322	0.375	540
$x = 2$	0.337	0.363	615
$x = 3$	0.358	0.358	614
$x = 4$	0.423	0.356	614
$x = 5$	0.595	0.398	615
$x = 6$	0.618	0.383	615





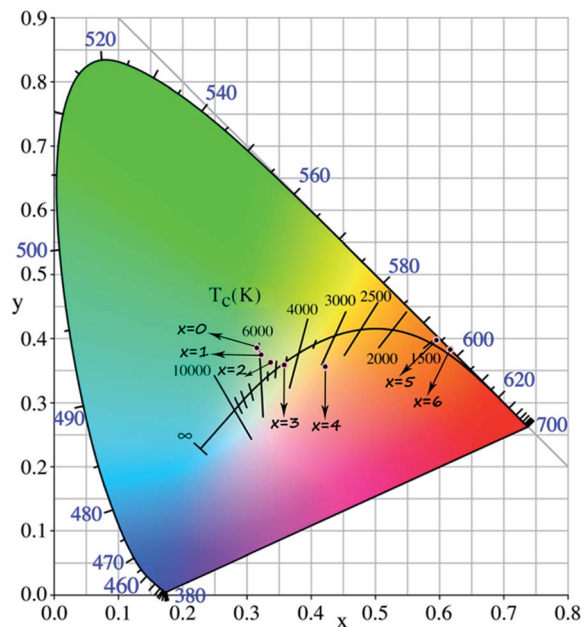


Fig. 3 CIE diagram of  $\text{Ca}_{(8-x)}\text{La}_{(2+x)}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2:2\% \text{Eu}$  (CLPSO- $x$ ) ( $0 \leq x \leq 6$ ) samples ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ).

single-activator-doped single-phased white light phosphors. The cation-cosubstitution derived.

$\text{Eu}^{2+}/\text{Eu}^{3+}$ -tunable strategy could be employed to design the desired single-phased white light in the apatite system.

To further verify the valence transformation of Eu in CLPSO- $x$ , a powerful evidence, namely, the normalized Eu  $L_3$ -edge extended X-ray absorption fine structure (XANES) spectra of the studied samples were collected in Fig. 4a.<sup>20,32</sup> Clearly, two peaks at 6975 eV and 6985 eV are observed, which are attributed to the electron transitions of  $2p_{3/2} \rightarrow 5d$  in  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , respectively.<sup>20,32</sup> The reason is the bigger shielding effect of nuclear potential by an additional 4f electron in  $\text{Eu}^{2+}$  than that in  $\text{Eu}^{3+}$ . For the CLPSO-0, Eu almost exists in the form of 2+ except for a small amount of residual  $\text{Eu}^{3+}$ , and this finding is consistent with the PL results. Moreover, the obviously higher emission of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  at 613 nm with respect to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  emission at 588 nm indicates that the  $\text{Eu}^{3+}$  ions mainly enter the deviating inverse symmetry crystalline sites.<sup>32,36</sup> For the substitution of  $[\text{Ca}^{2+}-\text{P}^{5+}]$  for  $[\text{La}^{3+}-\text{Si}^{4+}]$ , the absorption intensity of  $\text{Eu}^{2+}$  systematically increases, while that of  $\text{Eu}^{3+}$  correspondingly decreases, as shown in Fig. 4a. Finally, the Eu almost evolves to the 3+ format  $x = 6$ . The results convincingly demonstrate that  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  could coexist and mutually transform through the cation cosubstitution. A possible transformation mechanism between  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  is proposed, as shown by Fig. 4b. In the initial  $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$  lattices, the Eu ions preferentially occupy the  $\text{Ca}^{2+}$  (6h) sites, presenting the  $\text{Eu}^{2+}$  broad band emission. A moderate sintering temperature induces the mixing nanophases of  $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$  and  $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$  in the domain region, which further generates the multi-emitting sites of  $\text{Eu}^{2+}$  ions and produces a yellow-green emission. With the introduction of  $\text{Si}^{4+}$ , the  $\text{La}^{3+}$  ions at 6h sites simultaneously

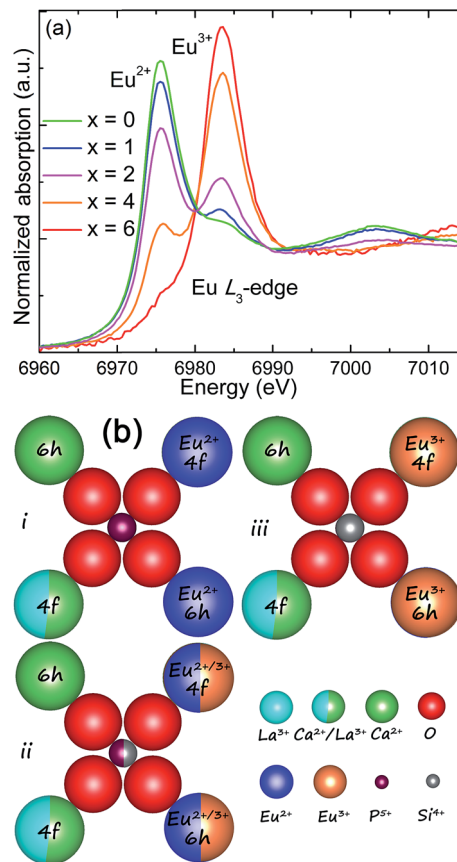


Fig. 4 (a) Normalized Eu  $L_3$ -edge X-ray absorption near edge structure (XANES) spectra of representative CLPSO- $x$  ( $x = 0, 1, 2, 4, 6$ ) samples. (b) A schematic mechanism to explain the transformation between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  with the cosubstitution of  $[\text{Ca}^{2+}-\text{P}^{5+}]$  for  $[\text{La}^{3+}-\text{Si}^{4+}]$ .

enter the  $\text{Ca}^{2+}/\text{Eu}^{2+}$  sites to balance charge, and thus  $\text{Eu}^{2+}$  ions gradually evolve to be  $\text{Eu}^{3+}$  ions. For the starting structure, the  $\text{La}^{3+}$  ions occupy all 6h sites and half of 4f sites in the ending  $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$  host. Therefore, the  $\text{Eu}^{2+}$  ions are finally completely transformed to  $\text{Eu}^{3+}$  ions. In general, the cation cosubstitution strategy could drive the coexistence and adjustment of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  in apatite structures, generating the single-phased white light phosphors for n-UV based WLEDs.

As an important index to evaluate the efficiency and stability of pc-WLEDs devices, the thermal quenching behaviour of CLPSO- $x$  samples from room temperature to 573 K was examined and shown in Fig. 5a.<sup>37-42</sup> Given a non-radiative transition under high working temperature, it is reasonable to observe the progressive emission attenuation of the studied samples.<sup>43-47</sup> It is noted that the thermal stability of  $x = 2-6$  samples are obviously better than that of  $x = 0, 1$  samples. Especially, a prominent improvement appears at  $x = 2$ , which can obtain 56% of the original emission intensity at room temperature. This is mainly because the outside electrons of Eu have a larger shielding effect for the 4f-4f transitions relative to its 5d-4f transitions.<sup>32,36</sup> Therefore, a weak electron-photon coupling interaction occurs and leads to a low thermal quenching under



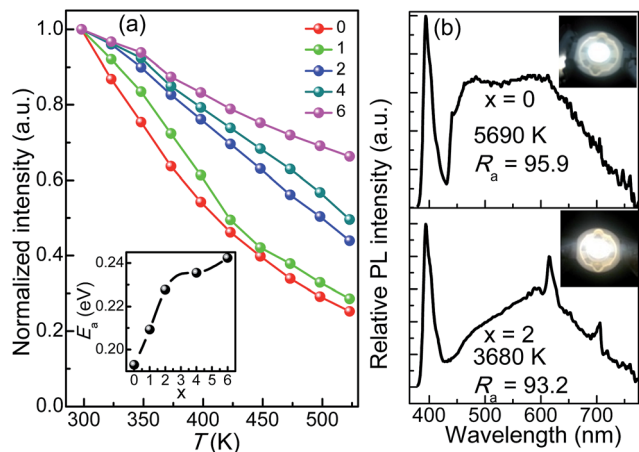


Fig. 5 Thermal quenching behaviour of photoluminescence for CLPSO- $x$  ( $x = 0$ – $6$ ) samples ( $\lambda_{\text{ex}} = 395$  nm). The insert shows the corresponding activation energy  $E_a$ . (b) Electroluminescence spectra of the CLPSO-0 (Top) and CLPSO-2 (Bottom) samples incorporated into an 395 nm-InGaN LED at 200 mA forward bias current. The CCT,  $R_a$  and corresponding luminescence photos (the insets) of the white lights are listed.

high temperature environment.<sup>32,36</sup> Finally, the  $x = 0$  and  $x = 2$  samples were fabricated to be single-phased white light-emitting devices combined with the 395 nm n-UV chips. Fig. 5b shows the corresponding electroluminescence (EL) spectra of the packaged WLEDs devices under a 200 mA forward bias current, which are basically in agreement with their PL results. Simultaneously, the packaged WLEDs present high  $R_a$  and low CCT, namely,  $R_a = 95.9$ , CCT = 5690 K for  $x = 0$  sample and  $R_a = 93.2$ , CCT = 3680 K for  $x = 2$  sample, respectively. The CIE color coordinates of  $x = 0$  and 2 samples are calculated to be (0.33, 0.33) and (0.38, 0.34), respectively. Therefore, excellent warm white light with high  $R_a$  could be realized in the single Eu-doped apatite phosphor by the cation cosubstitution.

## 4. Conclusions

In conclusions, a novel Eu-activated single-phased white light phosphor was developed based on the presence of multi-emitting  $\text{Eu}^{2+}$  and the transformation between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  by cation cosubstitution of  $[\text{La}^{3+}\text{--}\text{Si}^{4+}]$  for  $[\text{Ca}^{2+}\text{--}\text{P}^{5+}]$  in apatite analogue. The XRD patterns demonstrate that the formation of  $\text{Ca}_{8-x}\text{La}_{2+x}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}_2\text{:}2\% \text{Eu}$  solid solutions. Ultra broad  $\text{Eu}^{2+}$  emission from 420 nm to 600 nm imply the mixing nanophases of  $\text{Ca}_8\text{La}_2\text{Eu}(\text{PO}_4)_6\text{--}x(\text{SiO}_4)_x\text{O}_2$  samples at different sintering temperatures. The PL and XANES spectroscopy of Eu  $\text{L}_3$  edge convincingly confirm the valence transformation from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  by the substitution of  $[\text{La}^{3+}\text{--}\text{Si}^{4+}]$  for  $[\text{Ca}^{2+}\text{--}\text{P}^{5+}]$ . Because of a whole cover across the blue, green emission from  $\text{Eu}^{2+}$  and red emission from  $\text{Eu}^{3+}$  in CLSPO phosphors, we obtained high  $R_a$  warm white lights (95.9 for  $x = 0$ ; 93.2 for  $x = 2$ ), with the corresponding CCT of 5690 K and 3680 K, respectively. The newly developed single Eu-activated white light phosphors exhibit potential applications in single-phase white emitting n-UV pumped LEDs devices.

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## Notes and references

- 1 N. C. George, K. A. Denault and R. Seshadri, *Annu. Rev. Mater. Res.*, 2013, **43**, 481–501.
- 2 F. W. Kang, X. B. Yang, M. Y. Peng, L. Wondraczek, Z. J. Ma, Q. Y. Zhang and J. R. Qiu, *J. Phys. Chem. C*, 2014, **118**, 7515–7522.
- 3 C. H. Huang, T. W. Kuo and T. M. Chen, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1395–1399.
- 4 P. F. Smet, A. B. Parmentier and D. Poelman, *J. Electrochem. Soc.*, 2011, **158**, R37–R54.
- 5 N. Guo, Y. H. Zheng, Y. C. Jia, H. Qiao and H. P. You, *J. Phys. Chem. C*, 2012, **116**, 1329–1334.
- 6 C. H. Huang, Y. C. Chiu, Y. T. Yeh, T. S. Chan and T. M. Chen, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6661–6667.
- 7 K. Li, M. M. Shang, H. Z. Lian and J. Lin, *J. Mater. Chem. C*, 2016, **4**, 5507–5530.
- 8 Z. J. Wang, P. L. Li, Z. P. Yang and Q. L. Guo, *J. Lumin.*, 2014, **151**, 170–175.
- 9 P. L. Li, Z. J. Wang, Z. P. Yang and Q. L. Guo, *RSC Adv.*, 2014, **4**, 27708–27713.
- 10 W. R. Liu, C. H. Huang, C. W. Yeh, Y. C. Chiu, Y. T. Yeh and R. S. Liu, *RSC Adv.*, 2013, **3**, 9023–9028.
- 11 X. Ding, G. Zhu, Q. Wang and Y. H. Wang, *RSC Adv.*, 2015, **5**, 30001–30004.
- 12 P. P. Dai, C. Li, X. T. Zhang, J. Xu, X. Chen, X. L. Wang, Y. Jia, X. J. Wang and Y. C. Liu, *Light: Sci. Appl.*, 2016, **5**, e16024.
- 13 R. J. Xie and N. Hirotsaki, *Sci. Technol. Adv. Mater.*, 2007, **8**, 588–600.
- 14 P. Pust, V. Weiler, C. Hecht, A. Tücks, A. S. Wochnik, A.-K. Henß, D. Wiechert, C. Scheu, P. J. Schmidt and W. Schnick, *Nat. Mater.*, 2014, **13**, 891–896.
- 15 X. J. Zhang, J. Wang, L. Huang, F. J. Pan, Y. Chen, B. F. Lei, M. Y. Peng and M. M. Wu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10044–10054.
- 16 W. R. Liu, C. W. Yeh, C. H. Huang, C. C. Lin, Y. C. Chiu, Y. T. Yeh and R. S. Liu, *J. Mater. Chem.*, 2011, **21**, 3740–3744.
- 17 D. J. Hou, C. M. Liu, X. M. Ding, X. J. Kuang, H. B. Liang, S. S. Sun, Y. Huang and Y. Tao, *J. Mater. Chem. C*, 2013, **1**, 493–499.
- 18 Z. Y. Zhao, Z. G. Yang, Y. R. Shi, C. Wang, B. T. Liu, G. Zhu and Y. H. Wang, *J. Mater. Chem. C*, 2013, **1**, 1407–1412.
- 19 Q. Q. Zhu, L. Wang, N. Hirotsaki, L. Y. Hao, X. Xu and R. J. Xie, *Chem. Mater.*, 2016, **28**, 4829–4839.
- 20 K. W. Huang, W. T. Chen, C. I. Chu, S. F. Hu, H. S. Sheu, B. M. Cheng, J. M. Chen and R. S. Liu, *Chem. Mater.*, 2012, **24**, 2220–2227.
- 21 F. P. Du, Y. Nakai, T. Tsuboi, Y. L. Huang and H. J. Seo, *J. Mater. Chem.*, 2011, **21**, 4669–4678.



- 22 Y. S. Liu, W. Q. Luo, R. F. Li, G. K. Liu, M. R. Antonio and X. Y. Chen, *J. Phys. Chem. C*, 2009, **113**, 5340.
- 23 Z. G. Xia, G. K. Liu, J. G. Wen, Z. G. Mei, M. Balasubramanian, M. S. Molokeev, L. C. Peng, L. Gu, D. J. Miller, Q. L. Liu and K. R. Poeppelmeier, *J. Am. Chem. Soc.*, 2016, **138**, 1158–1161.
- 24 Z. G. Xia, C. G. Ma, M. S. Molokeev, Q. L. Liu, K. Rickert and K. R. Poeppelmeier, *J. Am. Chem. Soc.*, 2015, **137**, 12494–12497.
- 25 W. B. Im, N. George, J. Kurzman, S. Brinkley, A. Mikhailovsky, J. Hu, B. F. Chmelka, S. P. DenBaars and R. Seshadri, *Adv. Mater.*, 2011, **23**, 2300–2305.
- 26 M. Seibald, T. Rosenthal, O. Oeckler and W. Schnick, *CRC Crit. Rev. Solid State Sci.*, 2014, **39**, 215–229.
- 27 W. B. Park, S. P. Singh and K. S. Sohn, *J. Am. Chem. Soc.*, 2014, **136**, 2363–2373.
- 28 F. W. Kang, H. S. Zhang, L. Wondraczek, X. B. Yang, Y. Zhang, D. Y. Lei and M. Y. Peng, *Chem. Mater.*, 2016, **28**, 2692–2703.
- 29 Y. Sato, H. Kato, M. Kobayashi, T. Masaki, D. H. Yoon and M. Kakihana, *Angew. Chem., Int. Ed.*, 2014, **53**, 7756–7759.
- 30 W. T. Chen, H. S. Sheu, R. S. Liu and J. P. Attfield, *J. Am. Chem. Soc.*, 2012, **134**, 8022–8025.
- 31 D. G. Deng, H. Yu, Y. Q. Li, Y. J. Hua, G. H. Jia, S. L. Zhao, H. P. Wang, L. H. Huang, Y. Y. Li, C. X. Li and S. Q. Xu, *J. Mater. Chem. C*, 2013, **1**, 3194–3199.
- 32 G. G. Li, C. C. Lin, Y. Wei, Z. W. Quan, Y. Tian, Y. Zhao, T. S. Chan and J. Lin, *Chem. Commun.*, 2016, **52**, 7376–7379.
- 33 M. M. Shang, G. G. Li, D. L. Geng, D. M. Yang, X. J. Kang, Y. Zhang, H. Z. Lian and J. Lin, *J. Phys. Chem. C*, 2012, **116**, 10222–10231.
- 34 Y. F. Xia, J. Chen, Y. G. Liu, M. S. Molokeev, M. Guan, Z. H. Huang and M. H. Fang, *Dalton Trans.*, 2016, **45**, 1007–1015.
- 35 G. S. R. Raju, J. Y. Park, H. C. Jung, B. K. Moon, J. H. Jeong and J. H. Kim, *J. Electrochem. Soc.*, 2011, **158**, J20–J26.
- 36 F. W. Kang, Y. Zhang and M. Y. Peng, *Inorg. Chem.*, 2015, **54**, 1462–1473.
- 37 P. Dorenbos, *ECS Solid State Lett.*, 2013, **2**, R3001–R3011.
- 38 W. R. Liu, C. W. Yeh, C. H. Huang, C. C. Lin, Y. C. Chiu, Y. T. Yeh and R. S. Liu, *J. Mater. Chem.*, 2011, **21**, 3740–3744.
- 39 H. Daicho, T. Iwasaki, K. Enomoto, Y. Sasaki, Y. Maeno, Y. Shinomiya, S. Aoyagi, E. Nishibori, M. Sakata, H. Sawa, S. Matsuishi and H. Hosono, *Nat. Commun.*, 2012, **3**, 1132.
- 40 K.-S. Sohn, B. Lee, R.-J. Xie and N. Hirotsaki, *Opt. Lett.*, 2009, **34**, 3427–3430.
- 41 X. Piao, K. Machida, T. Horikawa, H. Hanzawa, Y. Shimomura and N. Kijima, *Chem. Mater.*, 2007, **19**, 4592–4599.
- 42 W. J. Zhou, F. J. Pan, L. Zhou, D. J. Hou, Y. Huang, Y. Tao and H. B. Liang, *Inorg. Chem.*, 2016, **55**, 10415–10424.
- 43 T. Takeda, N. Hirotsaki, S. Funahashi and R. J. Xie, *Chem. Mater.*, 2015, **27**, 5892–5898.
- 44 C. W. Yeh, W. T. Chen, R. S. Liu, S. F. Hu, H. S. Sheu, J. M. Chen and H. T. Hintzen, *J. Am. Chem. Soc.*, 2012, **134**, 14108–14117.
- 45 M. Y. Peng, X. W. Yin, P. A. Tanner, M. G. Brik and P. F. Li, *Chem. Mater.*, 2015, **27**, 2938–2945.
- 46 Y. Zhang, X. M. Liu, X. J. Li, K. Li, H. Z. Lian, M. M. Shang and J. Lin, *Dalton Trans.*, 2015, **44**, 7743–7747.
- 47 F. W. Kang, M. Y. Peng, D. Y. Lei and Q. Y. Zhang, *Chem. Mater.*, 2016, **28**, 7807–7815.

